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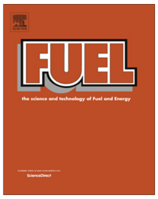

Bamboo pyrolysis using TG–FTIR and a lab-scale reactor: Analysis of pyrolysis behavior, product properties, and carbon and energy yields

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HIGHLIGHTS

- Typical compounds are identified by their characteristic absorbance in 3D FTIR.
- The absorbance changes of volatiles during pyrolysis agree with the DTG curve.
- Biochar yield decreases while gas yield increases with increased temperature.
- Biochar is the primary product as it has 41% or higher carbon and energy yields.
- Bio-oil and gas have 50–60% of carbon and energy yields when temperature is >400 °C.

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ABSTRACT

Slow pyrolysis of moso bamboo was performed using thermogravimetry–Fourier transform infrared analysis (TG–FTIR) and a laboratory-scale pyrolysis reactor. The effects of temperature on slow pyrolysis behavior, product properties, and carbon and energy yields at pyrolysis temperatures of 300–700 °C were discussed. Typical compounds such as CO_2, H_2O, CH_4, and CO were identified by their characteristic absorbance. The changes in the absorbance of volatiles during pyrolysis agreed with the weight loss in the derivative thermogravimetric curve. With increased temperature, biochar yield decreased while non-condensable gas yield increased. The bio-oil achieved the highest yield of 36.57% at 500 °C. Biochar was considered the primary product of pyrolysis because it had 41% or higher carbon and energy yields. Bio-oil and non-condensable gas contained 50–60% of carbon and energy content when the pyrolysis temperature was >400 °C. Therefore, these three types of products as valuable resources should be developed together for utilization.

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1. Introduction

Bamboo is a biomass material with the advantages of fast growth and high strength. According to statistics from the state forestry administration of China, China's bamboo forest area is 6.72 million hectares in 2011, accounting for 21% of the world's bamboo forest area. Moso bamboo, which accounts for about 47% of the Chinese bamboo forest area, is the most common bamboo plant in China. This bamboo can reach heights of up to 28 m. Bamboo especially the moso bamboo is widely used in building materials, green food, health care, furniture, farm tools, daily necessities, tourism souvenirs, and the landscape treatment, etc. In recent years, with the development of biomass energy, the thermochemical conversion utilization of moso bamboo is gaining increasing attention [1–11].

Table 1 presents recent studies in literature for pyrolysis of rice straw bamboo. The fast pyrolysis of bamboo and its components has been principally investigated for bio-oil production by using Py-GC/MS analysis [1–6]. Pyrolysis temperature markedly influences the product distribution of moso bamboo and enzymatic/mild acidolysis lignin by affecting the volatile yield and secondary cracking of heavy compounds [2,3]. Aromatic compounds and furans further crack into lighter products with increasing pyrolysis temperature [2,3,5]. 500 °C is found as an inflection point for product release during moso bamboo pyrolysis [5]. The three reactions are involved in bamboo pyrolysis in a fluidized-bed pyrolysis reactor: pyrolysis of exterior bamboo, pyrolysis of interior bamboo, and secondary pyrolysis of heavy tar [6].

Compared with fast pyrolysis, slow pyrolysis of bamboo is generally performed at a heating rate of 1–30 °C/min within the temperature range of 300–700 °C [5–11]. This means that a long time of approximately 1 h will require reaching the target temperature. Thermogravimetric analysis has been widely used to analyze

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slow pyrolysis of bamboo because of its advantages of minimal material requirement, simple operation, temperature program control, and online recording of mass loss. The derivative of mass loss from thermogravimetric data (DTG) has shown that the main pyrolysis occurs at 250–400 °C and that the solid product yield decreases from 25% to 17% at 400–700 °C [6]; and that the six-component model using a Runge–Kutta solution methodology is preferred in describing bamboo pyrolysis [8]. Fourier transform infrared analysis of the gas evolved TGA study has shown that H_2O, CH_4, CO_2, acids, and aldehydes are the principal volatile products of pyrolysis [11]. Kinetics analysis has elucidated that raw moso bamboo has an activation energy of 164.3 kJ mol^{-1} using a 3D diffusion model [5] and that the activation energy values of moso bamboo increase with heating rate [9]. Thermogravimetric–differential thermal analysis (TG–DTA) has also revealed that each bamboo component has a major decomposition step to volatile (endothermic) and a minor step resulting in char and gas (exothermic) [7].

These previous studies focused on the thermal decomposition of bamboo. However, the pyrolysis behaviors of moso bamboo, especially the volatile release profiles at different temperature, have not been fully investigated. TG–FTIR is a useful technology for obtaining mass loss with time and evaluating the functional groups of the volatile matter produced by pyrolysis [12,13]. Therefore, the present research first determines the effects of temperature on bamboo pyrolysis behavior using TG–FTIR.

Moreover, the products of biomass pyrolysis can be typically divided into bio-oil, char, and non-condensable gas. Bio-oil is a renewable fuel that can be upgraded into bio-fuels or used to produce value-added chemicals [14]. Non-condensable gas is principally composed of H_2, CO, and CO_2, which can be burned for energy recovery or used to produce syngas [15,16]. The amounts of bio-oil and energy content of non-condensable gases are larger than that of biochar [17]. Thus, the product properties of bio-oil and non-condensable gas need to be highly investigated. This requires comprehensive information on the properties and distribution of moso bamboo products at different pyrolysis temperatures. However, such information is limited in slow pyrolysis studies of bamboo in the literature, including those summarized in Table 1.

This study performed slow pyrolysis experiments of moso bamboo using TG–FTIR for the mass loss and volatile analysis of moso bamboo. To collect pyrolysis products and analysis of the typical gas product, slow pyrolysis experiments were performed using a laboratory-scale pyrolysis reactor that can approximate linear heating up. Base on these results, we discuss the production distribution, elemental composition, and carbon and energy yields of the three pyrolysis products (biochar, bio-oil, and non-condensable gas) at 300–700 °C.

2. Materials and methods

2.1. Feedstock materials

Moso bamboo is common in China, with an annual yield of about 18 million tons [11]. Moso bamboo (*Phyllostachys edulis*) was obtained from the Xiashu internship forest farm of Nanjing Forestry University. The bamboo was first sectioned into small pieces. As there were a bit of dirt and dust on the face of bamboo, these small pieces were washed using deionized water in order to eliminate the effect of the impurities on the pyrolysis experiments. These small pieces of bamboo were dried at 110 °C for 6 h, and then they were grinded by a multifunctional disintegrator (DS-Y500A, Zhuokai electric appliance, China). Finally, the bamboo particles were sieved by 40 mesh and 60 mesh sieves. The bamboo particles with a size of 0.38–0.25 mm were obtained, which were used as experimental materials. The moisture content of the sample was measured as 0.57 wt.%.

2.2. TG–FTIR analysis

Moso bamboo pyrolysis was performed using a TG–FTIR instrument that consists of a thermogravimetric analyzer (TGA Q500, TA Instrument, USA) and a Fourier-transform infrared spectrometer (Nicolet 6700, Thermo Scientific, USA). A sample mass of 19–21 mg was used in this study. The sample was heated from 30 °C to 700 °C at nitrogen flowing rate of 70 mL/min and a heating rate of 10 °C/min. The stainless steel transfer pipe and the gas cell in the FTIR were both heated at a constant temperature of 200 °C to minimize secondary reactions. The volatiles released during the pyrolysis of moso bamboo and their blends were detected online by FTIR, in which IR spectra were recorded at 4000–400 cm^{-1} with a resolution of 1 cm^{-1}. The experimental results of TGA and FTIR were recorded automatically by a computer.

Table 1
Recent studies on pyrolysis of bamboo and its components reported in literature.

Materials	Bamboo species	Reference	Pyrolysis type	Reactor type	Temperature	Heating rate	Key results
Bamboo	–	[1]	Fast	Py-GC/MS	600 °C	–	Component analysis of bio-oil
Lignin (EMAL)	Moso bamboo	[2]	Fast	Py-GC/MS	320–800 °C	10 °C/ms	Component analysis of bio-oil
Lignin (EMAL)	Moso bamboo	[3]	Fast	Py-GC/MS	250–800 °C	10 °C/ms	Component analysis of bio-oil
Bamboo	–	[4]	Fast	Fixed bed	<877 °C	–	Steam pyrolysis; properties of bio-oil, biochar and gas
Bamboo	Moso bamboo	[5]	Slow, fast	TG–FTIR, Py-GC/MS	30–850 °C, 400–700 °C	20 °C/min, 20 °C/ms	Typical absorbance peaks of pyrolysis products; component analysis of bio-oil
Bamboo	–	[6]	Slow, fast	TGA, fluidized-bed	25–700 °C, 400–700 °C	100 °C/min, –	Properties of bio-oil, biochar and gas
Bamboo	–	[7]	Slow	TG–DTA	25–800 °C	5–30 °C/min	Mathematical model for pyrolysis
Bamboo	–	[8]	Slow	TGA	150–500 °C	1–20 °C/min	Reaction models for pyrolysis
Bamboo	–	[9]	Slow	TGA	200–500 °C	1–20 °C/min	Kinetic parameters (*E* and *A*)
Bamboo	Iron bamboo	[10]	Slow	Fixed bed	300–900 °C	3 °C/min	Physical properties of monolithic carbons
Bamboo	Moso bamboo	[11]	Slow	TG–FTIR	50–550 °C	10 °C/min	Kinetic parameters; typical absorbance peaks of pyrolysis products
Bamboo	Moso bamboo	This study	Slow	TG–FTIR, fixed bed	30–700 °C, 400–700 °C	10 °C/min	Typical absorbance peaks of pyrolysis products; carbon and energy yields; properties of biochar, bio-oil, and gas

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2.3. Slow pyrolysis set-up

Slow pyrolysis experiments of moso bamboo were conducted using a laboratory-scale pyrolysis reactor (Fig. 1). In each test, approximately 50 g of the moso bamboo (moisture content 0.57 wt.% on wet base) was used. The sample was heated from 30 °C to different target temperatures (300, 400, 500, 600, or 700 °C) at a heating rate of 10 °C/min and then maintained for 10 min. Thermocouple was inserted into the sample, and the sample temperature was recorded every 2 min. Nitrogen (500 mL/min) was used to purge pyrolysis vapors from the reactor. The pyrolysis liquid product (bio-oil) was collected in the collector, and non-condensable gas was collected in a gas bag. After the experiment, the furnace was cleaned up, and biochar was collected.

Heating rate is an important factor that affects biomass pyrolysis. It is ease to achieve the linear heating rate of the sample in TGA. However, it is impossible to achieve the ideal linear heating rate in the fixed bed pyrolysis reactor, because the heating effect of the 50 g sample on the environment cannot be ignored. More time is needed at the beginning and end of the experiment. Fig. 2 shows the temperature curves which are the actual temperature changes during pyrolysis experiment in the laboratory-scale pyrolysis reactor. It can be observed that the linear heating conditions were basically established in the most of experiment process, and the sample was heated at approximate constant heating rate.

Biomass pyrolysis is a complicated heat and mass transfer process. Heating rate is an important factor that affects biomass pyrolysis. It is ease to achieve the linear heating rate of the sample in TGA, as only 20 mg of samples are used. However, it is very difficult to achieve the ideal linear heating rate in the fixed bed pyrolysis reactor, because the heating effect of the 50 g sample on the environment cannot be ignored. More time is needed at the beginning and end of the experiment. Fig. 2 shows the temperature curves which are the actual temperature changes during pyrolysis experiment in the laboratory-scale pyrolysis reactor. It can be observed that the sample was heated at approximate constant heating rate in the middle of experiment process, but at the beginning and the end of the experiment process, the heating rate of the sample were lower than 10 °C/min.

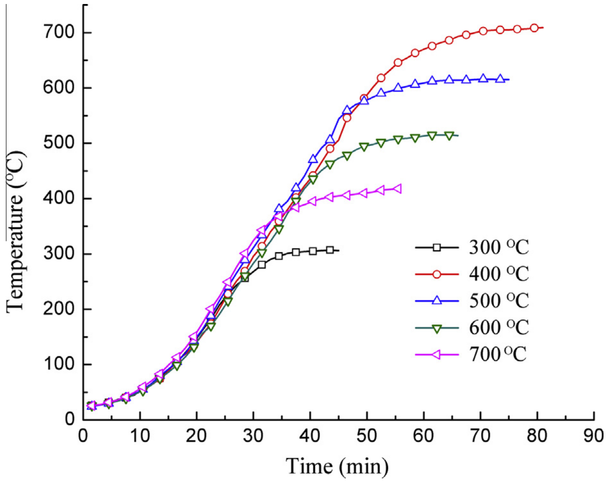

Fig. 2. Temperature profiles of bamboo in the laboratory-scale pyrolysis reactor.

2.4. Analytical methods

Proximate analysis was performed according to ASTM D3172-07a. Ultimate analysis was carried out using an elemental analyzer (Vario macro cube, Elementar, Germany), and oxygen was estimated by the difference. The higher heating values (HHVs) of biochar and bio-oil were measured in an adiabatic oxygen bomb calorimeter (XRY-1A, Changji Geological Instruments, China). The contents of hemicellulose, cellulose, and lignin were determined by the modified Van Soest method [18]. The specific surface area of biochar was determined using an automatic surface area and pore analyzer (Quandasorb SI, Quantachrome, USA). The water content in the bio-oil was determined by Karl–Fisher titration (SKF-1, Shanghai Super Scientech, China).

The physical and chemical properties of moso bamboo and its pyrolysis products (biochar, bio-oil and non-condensable gas) were analyzed. All the analysis experiments were replicated three times. The average of data and the standard deviation were listed in the Tables 2–5.

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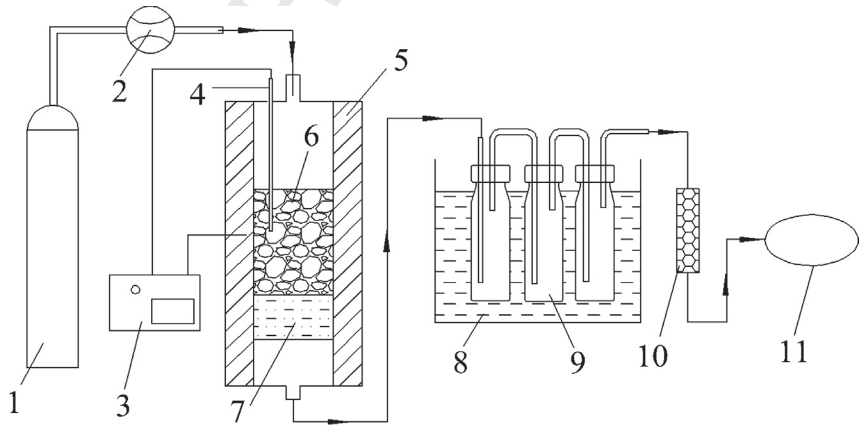

(1) Nitrogen supplier, (2) Flowmeter, (3) Temperature controller, (4) Thermocouple, (5) Pyrolysis furnace, (6) Feedstock, (7) Silicawool, (8) Condenser, (9) Bio-oil collector, (10) Drier, (11) Gas bag

Fig. 1. Illustration of the laboratory-scale pyrolysis reactor.

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3. Results and discussion

3.1. TG–FTIR analysis of moso bamboo

3.1.1. TG analysis

Moso bamboo has high carbon element content (47.20 wt.%) and volatile matter content (86.23 wt.%) but low sulfur element content (0.04 wt.%) and ash content (1.12 wt.%). The cellulose, hemicelluloses and lignin contents of moso bamboo are 41.35 wt.%, 29.56 wt.% and 23.27 wt.% on dry matter base, respectively. The HHV of moso bamboo is 16.63 MJ/kg. The TG results of moso bamboo at a heating rate of 10 °C/min are shown in Fig. 3. Pyrolysis consists of three stages: moisture evaporation (Stage I, 30–150 °C), main devolatilization (Stage II, 150–400 °C), and continuous slight devolatilization (Stage III, 400–700 °C). The mass loss during the moisture evaporation period was very little (0.54 wt.%) because the samples were dried before the pyrolysis experiments. The second stage involved fast devolatilization of the samples with large weight loss (68.72 wt.%). Cellulose, hemi-cellulose, and lignin behave differently during pyrolysis because of their chemical structures, and the temperatures at which cellulose and hemicellulose had peak volatilization were 287 and 333 °C, respectively [19]. The third stage involved the slow decomposition of residues with a slight weight loss (7.43 wt.%). Finally, biochar was formed upon the removal of the most volatile components.

3.1.2. 3D FTIR analysis

Fig. 4(a) shows the 3D FTIR spectra of volatiles evolved during moso bamboo pyrolysis at a heating rate of 10 °C/min. According to chemistry principles and some previous studies, typical compounds can be identified by their characteristic absorbance [20,21]. Fig. 4(b) shows the strongest characteristic absorbance at the time point of 31.3 min corresponding to DTG peak T_{max} = 323 °C. The bands between 4000 and 3400 cm^{-1} represent O—H bond stretching vibrations, related to H_2O, which came primarily from the evaporation and dehydration of the sample. The formation of CH_4, corresponding to the stretching vibration of C—H bonds at (3050–2650 cm^{-1}), can be caused by the cracking of the methoxyl (—O—CH_3), methyl (—CH_3), and methylene (—CH_2—) groups at <500 °C [22]. The rupture of aromatic rings was observed at 500 °C. The obvious characteristic absorbance at 2400–2240 cm^{-1} is representative of CO_2, which is mainly caused by the cracking and reforming of the functional groups of carboxyl (C=O) and carbonyl (C—O—C) [23]. The characteristic band of CO (2230–2000 cm^{-1}) is very close to that of CO_2. The release of CO can be attributed to the breakage of ether bonds and C=O bonds; the secondary decomposition of the volatiles and char residues at >600 °C can also form CO [24]. The most obvious characteristic absorbance is C=O stretching absorbance (1880–1620 cm^{-1}), which indicates the presence of aldehydes, ketones, and organic acids [25]. The bands at 1600–400 cm^{-1} are much complex, and identifying each component is difficult. Previous studies showed that these bands indicate the presence of some organics, including alcohols, aldehydes, acids, and phenols [24,26,27].

Table 2
Product yields of moso bamboo pyrolysis.

Temperature (°C)	Product yields (wt.%)		
	Biochar	Bio-oil	Non-condensable gas
300	49.3 ± 1.2	26.5 ± 0.8	23.2 ± 1.4
400	30.7 ± 0.7	35.2 ± 1.3	34.1 ± 1.5
500	26.0 ± 0.9	36.6 ± 1.1	37.4 ± 1.4
600	24.3 ± 1.1	36.1 ± 0.7	39.6 ± 1.3
700	23.6 ± 0.8	34.1 ± 0.9	42.3 ± 1.2

Absorbance and gas consent ratio show a linear relationship according to Beer–Lambert's law. Basing on this relationship, we can determine the variation in some components with increasing temperature. Fig. 4 shows that the changes in the absorbance of volatiles during pyrolysis agree with the weight loss in the DTG curve shown in Fig. 3. The first stage of pyrolysis occurs within 0–14.5 min (below 150 °C), and the weight loss is very minimal in TG. Accordingly, almost no compounds are found in the 3D FTIR. The characteristic bands of CO_2, H_2O, CH_4, and CO gradually appear and increase within 14.5–39.5 min (between 150 °C and 400 °C). Meanwhile, the organic species of furans, phenols, ketones, and aldehydes are generated. The strongest spectral intensity of the above components emerges after 32 min, which corresponds to the maximum weight loss rate in the DTG curve. The last stage of pyrolysis occurs within 39.5–69 min (>400 °C), and the absorbance gradually decreases.

It should be noted that the sample mass of 19–21 mg used in this study is larger than that used in TGA in numerous previous studies. In order to limit the effect of sample mass on the mass and heat transfer, 3–10 mg of sample was generally used. After many tests, it was found that 20 mg of samples can product a better 3D FTIR spectrum of volatiles. Actually, the manual of TG–FTIR also recommended using 20 mg sample; and a good results were found for bamboo pyrolysis by Jiang et al. when they used about 20 mg sample in TG–FTIR [11]. Thus, 19–21 mg of sample was used in TG–FTIR experiments.

The sample mass has a certain effect on biomass pyrolysis. High volume of biomass due to its low density of biomass made the heat and mass transfer limitation. The effect of sample mass was obvious in the slow pyrolysis experiments where the sample did not reach the desired temperature using the 10 °C/min heating rate in Fig. 2.

3.2. Product yields

Biochar and bio-oil were collected after the test and weighed to determine the yields. The gas yield was calculated by difference. Temperature is a key factor that influences bamboo pyrolysis and final products. Table 2 shows the product yields of pyrolysis at 300–700 °C. The biochar yield decreased with increasing temperature because of thermal decomposition, which results in increased gas yields. The biochar yield rapidly decreased from 49.3% to 30.7% at <400 °C, whereas the decrease at >400 °C was less than 7% because the decomposition of cellulose and hemicellulose was completed. The bio-oil yield achieved the highest, i.e., about 36.6%, at 500 °C.

3.2.1. Characteristics of non-condensable gas

The results of gas composition are shown in Table 3. The non-condensable gas was collected during the pyrolysis process. As shown in Table 3, CO_2 and CO are the dominant species. The contents of CH_4 and H_2 rapidly increased above 400 °C. C_{2+} hydrocarbons consists of 1.56 vol.% of C_2H_6, 0.82 vol.% of C_2H_4, 0.75 vol.% of C_3H_8, 0.73 vol.% of C_3H_6, 0.27 vol.% of C_4H_{10}, and 0.18 vol.% of C_4H_8 at the peak temperature of 600 °C. The HHVs of the non-condensable gas were obtained from the sum of the gas product concentrations and the high calorific value.

$$\begin{aligned} HHV_{gas}(MJ/Nm^3) = {} & Vol._{CO}(\%) \times HHV_{CO}(MJ/Nm^3) + Vol._{H2}(\%) \\ & \times HHV_{H2}(MJ/Nm^3) + Vol._{CH4}(\%) \\ & \times HHV_{CH4}(MJ/Nm^3) + Vol._{C2H6}(\%) \\ & \times HHV_{C2H6}(MJ/Nm^3) + \cdots + Vol._{C4H8}(\%) \\ & \times HHV_{C4H8}(MJ/Nm^3). \end{aligned}$$

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Table 3
Characteristics of non-condensable gas from different pyrolysis temperatures.

Temperature (°C)	Gas composition (vol.%)					HHV (MJ/N m^3)	HHV (MJ/kg)
	CO_2	CO	CH_4	H_2	C_{2+}		
300	66.7 ± 0.5	27.3 ± 0.7	1.6 ± 1.1	2.9 ± 0.1	1.5 ± 0.1	5.8 ± 0.5	3.6 ± 0.3
400	47.9 ± 0.8	36.3 ± 1.1	6.4 ± 0.4	8.1 ± 0.2	1.3 ± 0.1	9.2 ± 0.2	6.7 ± 0.2
500	41.3 ± 0.9	36.4 ± 1.2	11.8 ± 0.6	9.2 ± 0.5	1.3 ± 0.1	11.6 ± 0.3	9.1 ± 0.2
600	37.9 ± 1.1	33.5 ± 0.6	12.3 ± 0.8	14.2 ± 0.2	2.1 ± 0.1	12.8 ± 0.3	10.7 ± 0.3
700	33.4 ± 0.4	31.8 ± 0.5	13.7 ± 0.5	19.8 ± 0.3	1.3 ± 0.1	13.1 ± 0.2	11.9 ± 0.2

Table 4
Characteristics of bio-oil from different pyrolysis temperatures.

Temperature (°C)	Ultimate analysis (wt.%)					Water content (wt.%)	HHV (MJ/kg)
	C	H	N	S	O		
300	25.45 ± 1.06	10.16 ± 0.25	1.86 ± 0.12	0.12 ± 0.01	62.41 ± 1.10	65.2 ± 1.12	10.53 ± 0.5
400	29.58 ± 0.89	9.35 ± 0.62	2.07 ± 0.13	0.11 ± 0.01	58.89 ± 1.09	67.9 ± 1.05	13.95 ± 0.5
500	29.73 ± 0.36	8.93 ± 0.58	1.93 ± 0.08	0.13 ± 0.01	59.28 ± 0.69	68.3 ± 0.58	13.41 ± 0.5
600	29.36 ± 0.51	8.42 ± 0.53	1.95 ± 0.11	0.12 ± 0.01	60.15 ± 0.74	68.6 ± 0.83	12.49 ± 0.5
700	28.53 ± 0.32	8.41 ± 0.45	1.96 ± 0.05	0.11 ± 0.01	60.99 ± 0.55	68.9 ± 0.95	11.07 ± 0.5

According to the density of each gas, the overall gas density of the non-condensable gas can be obtained. Then, the HHVs of the non-condensable gas based on MJ/kg were calculated. Table 3 also shows the HHVs of gas composition. Compared with CO (10.1 MJ/kg), H_2 and CH_4 had higher HHVs (e.g., 141.8 MJ/kg for H_2 and 55.5 MJ/kg for CH_4). The increase in H_2 and CH_4 with increasing temperature directly increased the HHV from 3.6 MJ/kg (5.8 MJ/N m^3) at 300 °C to 11.9 MJ/kg (13.1 MJ/N m^3) at 700 °C.

3.2.2. Characteristics of bio-oil

The appearance of the pyrolytic liquid product (bio-oil) during the laboratory-scale pyrolysis reactor experiments was a homogeneous liquid. It was easy to analyze its properties. However, after several days of storage, the bio-oil underwent phase separation [28]. The supernatant liquid with water content as high as 70–85%, which we called light aqueous phase, generally accounted for 60–75% in the bio-oil. The elemental composition and HHV of the light aqueous phase were very different to determine because of the excess water that influenced instrument performance. By contrast, the underlayer liquid, which we called dark heavy phase, contained a small amount of water, had high carbon content (>60%), and had a high HHV (>25 MJ/kg).

There was not a specific point of time that the separation was complete. Generally, after seven days of storage, the supernatant liquid and the underlayer liquid were separated noticeably. In this study, after the pyrolysis experiments, the homogeneous bio-oil collected from pyrolysis reactor was analyzed as soon as possible. Its properties are summarized in Table 4. With increasing temperature, the water content increased while the HHV of bio-oil decreased. This high oxygen content and low carbon content indicates the low quality and value of the bio-oil.

3.2.3. Characteristics of biochar

Table 5 summarizes the properties of biochar. The percentages of carbon element and fixed carbon generally increased while those of volatile, hydrogen element, and oxygen element reduced with increasing temperature. This result indicates that the pyrolysis of solid products was enhanced with increasing temperature, which agrees with the results of TG experiments. As the pyrolysis temperature increased, the biochar became highly carbonaceous, with a carbon content range of 68.56–88.34 wt.%. This increase in temperature also increased the HHV from 25.43–29.56 MJ/kg.

Microscopic surface area is a crucial property of biochar. This property determines the capability of nutrients and water adsorption. The surface area of biochar increased from 12.31 m^2/g at 300 °C to >64.45 m^2/g at 700 °C. The surface area of the moso bamboo biochar is similar to that of straw biochar [29] at 500 °C but relatively low compared with that of biochar from lignocellulosic biomass, such as bagasse, wood stem, and palm kernel shell, at 500 °C [17].

3.2.4. Effect of secondary cracking

With increasing pyrolysis temperature, especially >500 °C, the bio-oil yield slightly decreased, whereas the water content increased. In addition, the yields of CO_2 and CO decreased, whereas those of H_2 and CH_4 increased. The decrease of the bio-oil yield and the changes of the gas products mainly attributed to the secondary cracking of the primary bio-oil compounds at high temperatures. In addition, the hot char acts as a catalyzer, which plays an important role in secondary cracking [30]. With the increasing of the pyrolysis temperature, less O remained in biochar. The decreased O content in the biochar mainly attributed to the temperature-promoted pyrolysis reactions on the remained biochar.

Table 5
The properties of biochar from different pyrolysis temperatures.

Temperature (°C)	Ultimate analysis (wt.%, db)					Proximate analysis (wt.%, db)			HHV (MJ/kg)	Specific surface area (m^2/g)
	C	H	N	S	O	Volatile matter	Fixed carbon	Ash		
300	68.56 ± 0.81	3.85 ± 0.11	0.92 ± 0.15	0.13 ± 0.01	26.54 ± 0.83	30.92 ± 0.81	65.16 ± 0.82	3.92 ± 0.12	25.43 ± 0.21	12.31 ± 0.58
400	74.64 ± 1.01	3.48 ± 0.09	0.94 ± 0.12	0.14 ± 0.02	20.8 ± 1.02	25.16 ± 0.35	71.51 ± 0.38	3.33 ± 0.15	27.46 ± 0.26	26.12 ± 1.02
500	79.12 ± 0.89	2.53 ± 0.05	1.03 ± 0.08	0.13 ± 0.01	17.19 ± 0.89	20.53 ± 0.56	75.39 ± 0.58	4.08 ± 0.17	28.15 ± 0.35	48.35 ± 1.25
600	83.95 ± 0.95	1.67 ± 0.03	1.01 ± 0.07	0.14 ± 0.01	13.23 ± 0.95	12.92 ± 0.43	82.83 ± 0.43	4.25 ± 0.09	28.97 ± 0.58	60.93 ± 0.93
700	88.34 ± 0.67	1.26 ± 0.08	1.06 ± 0.04	0.14 ± 0.01	9.20 ± 0.68	9.37 ± 0.72	86.37 ± 0.72	4.26 ± 0.11	29.56 ± 0.62	64.45 ± 0.98

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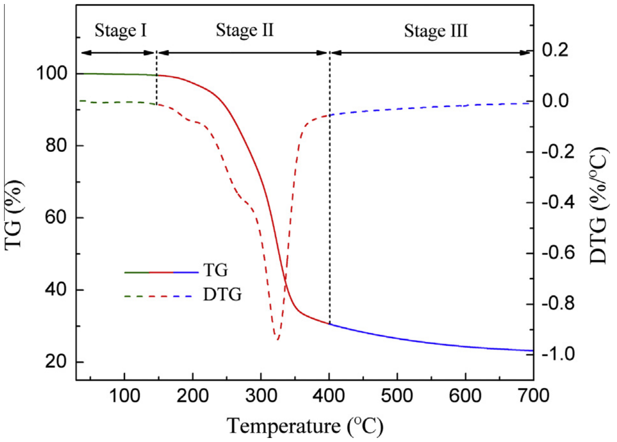

Fig. 3. TG and DTG curve of moso bamboo at heating rate of 10 °C/min.

This phenomenon is not obvious because the sample amount used in the reactor is only 50 g. However, in a large-scale test with a continuously operating pyrolysis process, the phenomenon could be significant because a large amount of hot char is formed and the volatiles need to pass though the hot char particles [31,32].

3.3. Carbon and energy distribution of the products

Base on the product yields and ultimate analysis, we can calculate the carbon yield representing the amount of carbon remaining in the pyrolysis products (bio-oil, biochar, and gas). Then, we can calculate the energy yield representing the amount of energy remaining in the pyrolysis products from the product yields and HHV values. Fig. 5 shows the distribution of carbon and energy between pyrolysis products (bio-oil, biochar, and non-condensable gas).

The total carbon and energy yields of the three products deviated by 1.1–5.1% and 2.7–5.2% from 100%, respectively. The deficiency was not significant probably because of experimental errors in the ultimate analysis of sample, bio-oil collection, and the error involved in the estimation of gas composition and HHV.

With increasing temperature, the carbon yield in biochar decreased. However, 44.11% of carbon in bamboo retained in the biochar at 700 °C. In previous studies for other biomass, biochar is the preferred product of carbon that condensed the amorphous

PROOF

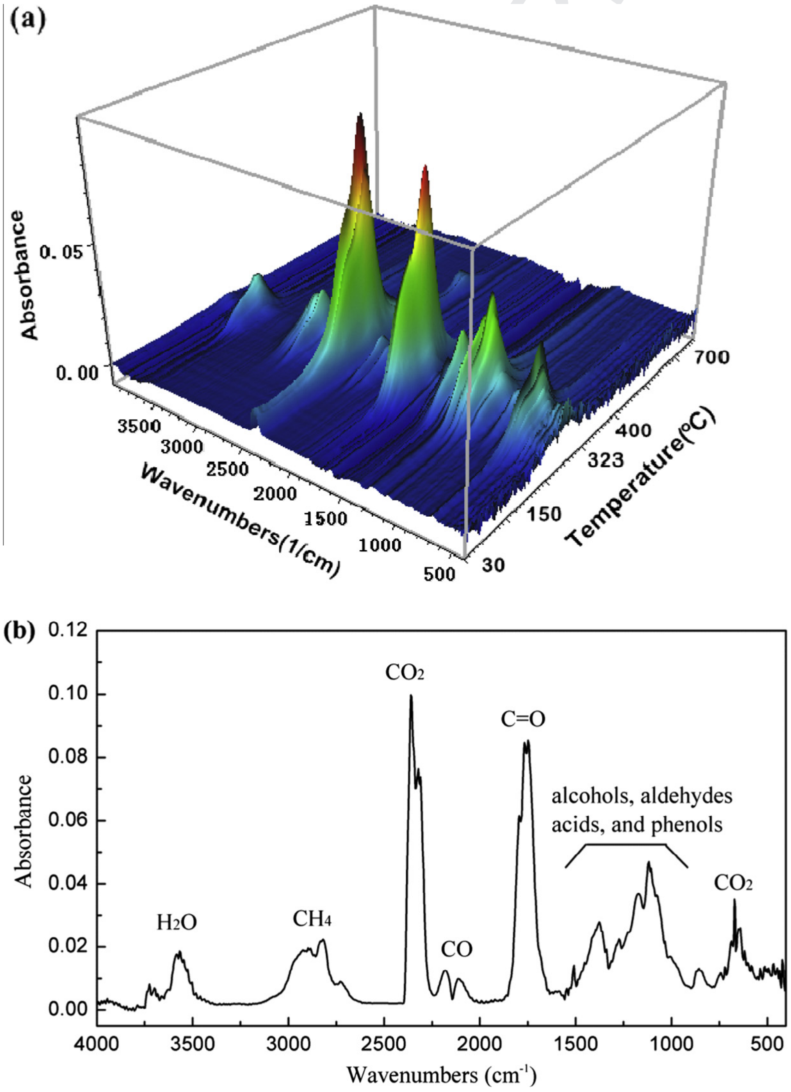

Fig. 4. Bamboo pyrolysis using TG–FTIR: (a) 3D infrared spectrum of pyrolysis products at heating rate of 10 °C/min and (b) FTIR spectrum for pyrolysis products corresponding to DTG peak T_{max} = 323 °C.

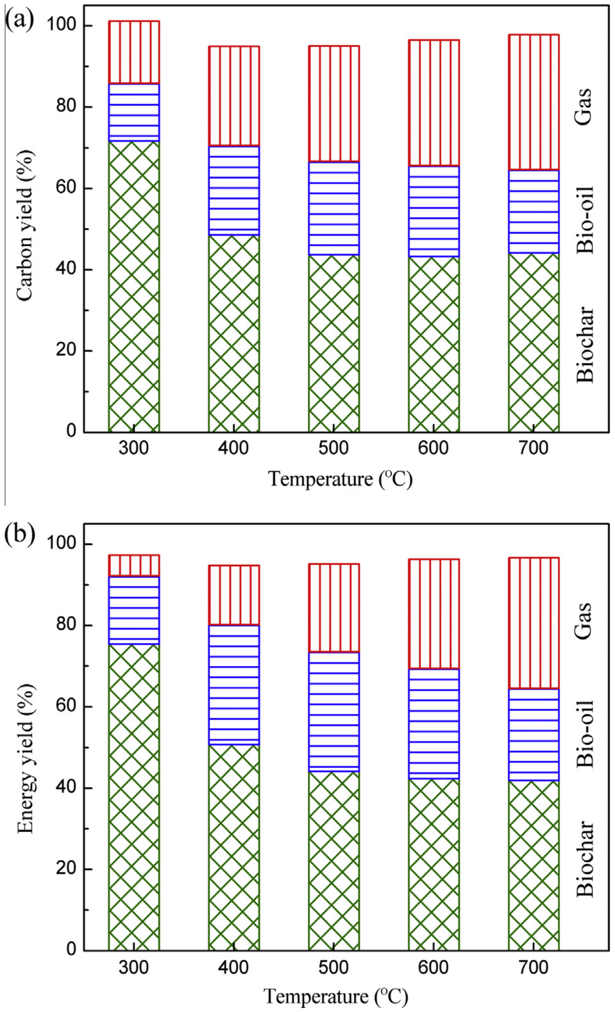

Fig. 5. Carbon and energy distribution between pyrolysis products of moso bamboo.

carbon structure with many functional groups and bridges into highly aromatic carbon skeletons [29]. In the present study, considering that the biochar yield was low (only about 23.57–26.05% over 500 °C) but had 41% or higher carbon and energy yields, we considered biochar to be the primary product of pyrolysis.

Bio-oil had carbon yields of 20.59–23.02% at >500 °C and energy yields of 22.71–29.49%. Although the mass yield of bio-oil was higher than that of biochar, its energy yield of bio-oil was lower than that of biochar.

The non-condensable gas seems the second important product. Its carbon yields are higher than those of bio-oil; at pyrolysis temperatures above 600 °C, its energy yields are higher than those of bio-oil. The HHV of non-condensable gas shown in Table 3 was calculated from the pyrolysis gas products (CO, H_2, CH_4, CO_2, and C_{2+}). However, the actual HHV of gas collected from pyrolysis experiment would be much lower because a large amount of the N used as a carrier gas also mixed in the non-condensable gas. An effective way to use the gas is to heat the pyrolysis reactor because biomass pyrolysis requires external heat supply. In some pilot plants of biomass pyrolysis in China, the gas is not directly discharged to the atmosphere but used in combustion instead of electric heating for the reactor.

Bio-oil and non-condensable gas, which contained 50–60% of carbon and energy content when the pyrolysis temperature was >400 °C, are the important products in bamboo pyrolysis. Therefore, these three types of products as valuable resources should be planned together for utilization.

4. Conclusions

Pyrolysis temperature remarkably influenced the volatile release profiles, product properties, and carbon and energy yields of moso bamboo. The secondary cracking of primary bio-oil compounds by temperature and by hot char surface was not obvious in this study. This phenomenon could be significant in the continuously operating pyrolysis process, because the volatiles need to pass though more hot char particles. Biochar was the primary product of pyrolysis. However, the by-products (bio-oil and non-condensable gas) should be planned together for utilization because the total carbon and energy yields were both more than 50% when the pyrolysis temperature was >400 °C.

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